

**REMARKS**

Claims 1-34 are pending in the application. The specification has been amended above to correct typographical errors. The claims have been amended above, without any change in scope or content, to correct typographical errors and to remove symbols inadvertently placed in the claims.

Applicants respectfully request entry of the foregoing amendments and examination of the application.

Respectfully submitted,  
Benton et al.

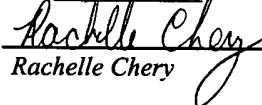


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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
(B & W Docket No. 003259.00016)

<b>Applicants:</b>	<b>Benton et al.</b>	<b>Paper No:</b>
<b>Serial No.:</b>	<b>09/918,410</b>	<b>Group Art Unit:</b>
<b>Filed:</b>	<b>July 30, 2001</b>	<b>Examiner:</b>
<b>Title:</b>	<b>Hydrophobe Associative Polymers and Compositions and Methods Employing Them</b>	

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**VERSION SHOWING CHANGES MADE**

**IN THE SPECIFICATION**

The paragraph beginning on page 11, line 12, is amended as shown below. The term "stericly" has been replaced with "sterically" to correct the typographical error.

The hydrophobe associative polymers may have any suitable polymeric form, including, for example, a linear, comb-like, or helical polymer form. Without wishing to be bound by theory, the hydrophobic moieties of the polymer are understood to be sufficiently ~~stericly~~sterically unhindered to associate with one another in sufficient degree when the polymer is in an aqueous medium and, more specifically, in a saturated aqueous solution of an alkali metal salt of a carboxylic acid, under low or no shear, thereby increasing the viscosity of the composition under those conditions. More specifically, and still not wishing to be bound by theory, it currently is understood that associative interactions between the hydrophobes in an aqueous medium, e.g., a saturated aqueous solution of cesium formate, contribute stability and viscosity while under low or no shear

conditions. Under such conditions, the associative interactions break and reform up to some yield point. Up to this point, the fluid exhibits viscoelastic behavior. At higher shear rates the aqueous polymer composition passes through a transition from viscoelastic and thixotropic to shear thinning behavior. After shear forces are released or removed, it will relax to its viscoelastic behavior. This reversible viscosity or thixotropic behavior allows relatively lower molecular weight polymer compositions disclosed here to attain higher viscosities in low shear regions of a well servicing operation and suffer relatively lower mechanical degradation at high shear.

The paragraph beginning on page 14, line 16, is amended as shown below. The second period at the end of the paragraph has been deleted.

As disclosed above, moiety R of the reactant preferably is substantially nonreactive with the AMPS reactant during preparation of the water soluble polymer. Without wishing to be bound by theory, it presently is understood that the double bond of the carbonyl reactant is reactive with the AMPS reactant, but that moiety R should be nonreactive at least in the sense that it does not covalently or ionically react with the AMPS reactant to cause the reaction product, i.e., the water soluble polymer, to be a three dimensional cross-linked polymeric network. In this regard, however, the R moieties of the water soluble polymer, in a use environment, are understood to be reactive with each other sufficiently to yield a hydrophobized water soluble polymer, that is, to provide a hydrophobic effect. Thus, while substantially nonreactive during preparation of the water soluble polymer, the R moieties provide a thixotropic, hydrophobized polymer

composition. In certain preferred embodiments, substantially no other reactants are used in forming the hydrophobe associative polymer other than the AMPS reactant, the carbonyl reactant and the hydrophobe reactant.-

The paragraph beginning on page 15, line 16, is amended as shown below. Numerous additional spaces between words have been deleted. The sentence enclosed in brackets has also been deleted. At page 16, line 3, the term "0.05wt." has been replaced with "0.05 wt." to correct the typographical error. At page 16, line 3, the term "2.0wt." has been replaced with "2.0 wt." to correct the typographical error. At page 16, line 4, the term "1.0wt." has been replaced with "1.0 wt." to correct the typographical error. At page 16, line 19, the term "425°F" has been replaced with "425 °F" to correct the typographical error.

Preferably the water soluble hydrophobe associative polymer is prepared as the reaction product of 2-acrylamido-2-methylpropanesulfonic acid or 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propanesulfonic acid or salt thereof, with, methacrylic acid, maleic acid, fumaric acid, acrylic acid or salt thereof, a methacrylate having a -COOR group where R is stearyl, lauryl, ethylhexyl or other C8 to C18 alkyl, or a mixture of any of them, and a minor amount of bifunctional cross-linking agent such as N,N'-methylenebis[2-propenamide or the like. The water soluble polymer preferably has about 5 to 95 wt. %, more preferably about 30 to 80 wt. % structural units derived from 2-acrylamido-2-methylpropanesulfonic acid or other AMPS reactant, about 5 to 95 wt. %, more preferably about 20 to 60 wt. % structural units derived from acrylic acid or other

carbonyl reactant, about ~~0.05 wt. %~~ 0.05 wt. % to ~~2.0 wt. %~~ 2.0 wt. %, more preferably about 0.2 wt. % to ~~1.0 wt. %~~ 1.0 wt. % structural units derived from alkylmethacrylate or other hydrophobe reactant, and about 0 to 5 wt. %, more preferably about 0 to 0.1 wt. % structural units derived from cross-linking agent. Preferred salts of the polymer include, for example, alkali metal salts, ammonium salts and the like. The molecular weight of preferred embodiments of the hydrophobe associative polymers disclosed here preferably is in a range suitable to be soluble and effective in well service fluids, preferably being soluble at least to the degree disclosed above in a saturated aqueous solution of an alkali metal salt, most preferably cesium formate. A saturated aqueous solution of cesium formate containing 1 ppb of preferred embodiments of the hydrophobe associative polymer can be subjected to a degree of shear on the order of  $10,000 \text{ sec}^{-1}$  at a temperature of  $400^\circ\text{F}$  without being degraded significantly. ~~{Eliminated because this test was not done in this patent, only the last patent.}~~ While embodiments of the associative polymers disclosed here having very high molecular weight, e.g., weight average molecular weight (MW) greater than 5 million, can be suitably employed, such polymers tend to degrade when subjected to high shear, e.g., shear in excess of  $10,000 \text{ sec}^{-1}$  - at elevated temperatures, e.g., temperatures up to ~~425°F~~ 425 °F. Accordingly, such polymers are less preferred for some applications. Preferred embodiments of the hydrophobe associative polymers have weight average molecular weights (MW) as determined by gel permeation chromatography in the range from about 200,000 to about 4 million, more preferably from about 1 million to about 3 million, most preferably from about 1,500,000 to about 3 million.

The paragraph beginning on page 17, line 21, is amended as shown below. Numerous spaces at the beginning of the paragraph have been removed. A comma has been removed after the word "contain" on page 18, line 8, of the specification.

———Compositions disclosed here, as already discussed above, comprise water soluble hydrophobe associative polymer and alkali metal salt of carboxylic acid. In accordance with one aspect, the hydrophobe associative polymer has functionality including at least sulfonate groups, carboxylate groups and hydrophobes associative with one another in a saturated aqueous solution of an alkali metal salt of a carboxylic acid. In accordance with another aspect, the hydrophobe associative polymer is a polymerization reaction product of reactants comprising AMPS reactant, alpha, beta-unsaturated carbonyl reactant and hydrophobe reactant as discussed above. It will be apparent to those skilled in the art that quantities of other ingredients suitable to the intended use may be present in the composition. For example, compositions intended for use in or as a well drilling or other well servicing fluid may also contain, salts such as sulfates, nitrates and bicarbonates, and other ingredients. Such salts will inevitably will be present where sea water or other naturally occurring brine is used in preparing the compositions. If desired, the hydrophobe associative polymer composition may also contain an antioxidant, e.g. 2-mercaptobenothiazole and/or other suitable additives. When 2-mercaptobenothiazole is used, it may be incorporated in the same proportion, w/v, as the water soluble polymer. Those skilled in the art will understand that 1% w/v corresponds to a concentration of 10kg/m<sup>3</sup> (10 g/l) of composition. It is generally preferred that the pH of hydrophobe associative polymer compositions intended for wellbore use be adjusted to pH 8.0 to pH

11.5, for reasons of stability and reduced corrosiveness of the composition. Most preferably, the pH should be in range of pH 9.0 to pH 10.5. The pH may be controlled by the addition of suitable reagents, for example, sodium hydroxide. The presence of a monovalent salt, such as a carbonate salt, e.g., potassium carbonate or cesium carbonate, in the composition can provide suitable pH buffering.

The paragraph beginning on page 21, line 3, is amended as shown below. The term "50%of," as recited on page 22, line 3, of the specification, has been replaced with the terms "50% of" to correct the typographical error.

The alkali metal salt of carboxylic acid used in the compositions disclosed here is preferably selected from sodium, potassium and cesium salts of suitable carboxylic acids, blended to obtain the desired density of the well service fluid. Preferably, acetates or, more preferably, formates are used. In accordance with certain preferred embodiments, the composition is 40 % w/w or higher cesium formate. In accordance with certain highly preferred embodiments, at least about 5 wt. % of the alkali metal salt of carboxylic acid is cesium formate. Such embodiments are found to provide well service fluids having advantageous density and durable rheological properties. In that regard, the cesium fluids at about 43 % of saturation are found to provide densities equal to the density of substantially saturated potassium brines. At concentrations higher than 43 %, the cesium fluids advantageously provide even higher densities, such as 2.18 - 2.3 sg. As noted above, it is a significant and unexpected advantage of the hydrophobe associative polymers disclosed here, that they are sufficiently water soluble to yield high, durable,

high-temperature viscosity suitable for well servicing fluids, in saturated or unsaturated solutions of alkali metal carboxylates. It is advantageous, for example, that the water soluble hydrophobe associative polymers disclosed above, having weight average molecular weight of 200,000 to 5,000,000 are soluble at least to levels of 0.05 to 5 wt. % (based on the weight of all solids contents of the composition) in an 80 % or higher brine of alkali metal carboxylate, yielding an apparent viscosity greater than or equal to 20 cPs., a plastic viscosity of greater than or equal to 15 cPs., and a yield point of greater than or equal to 5lb/100 ft<sup>2</sup> when dissolved in alkali metal formate brine solution at a concentration of 2 pounds per barrel and measured at 120 degrees F. Moreover, this advantageous rheology is durable, in that the aqueous hydrophobized polymeric compositions retain at least ~~50%~~50% of its apparent viscosity after roller aging for 30 days at 375 degrees F and measured at 120 degrees F.

The paragraph beginning on page 24, line 24, is amended as shown below. The term "was added," as recited on page 24, line 24, has been replaced with "was added" to correct the typographical error. The term "sample was then," as recited on page 24, line 27 of the specification, has been replaced with "sample was then" to correct the typographical error.

In samples 4-7 where N Vis HB is used, the N Vis HB ~~was added~~was added to the cesium formate base solution and stirred on a Waring Blender for five minutes. Next, the hydrophobe associative polymer was slowly added to the solution while stirring on a Hamilton Beach mixer. Each ~~sample was then~~sample was then poured into a stainless



steel "bomb" (a 350 ml lab barrel) and hot-rolled for 16 hours at 150° F in accordance with the aforesaid API test procedures. After 16 hours, the samples were cooled down to 120° F and the viscosities were read using a FANN 35 viscometer. The viscosities were read at several different rpm settings to calculate the plastic viscosity and yield point of each sample. The results are listed in Table 2 below.

The paragraph beginning on page 26, line 11, is amended as shown below. The term "was added", as recited on page 26, line 11 of the specification, has been replaced with "was added" to correct the typographical error.

Next, 40 pounds per barrel of LoWate calcium carbonate ~~was added~~was added to each of the sample solutions. LoWate is the trade name for commonly available M-I drilling fluids CaCO<sub>3</sub> additive. The viscosity of each sample was again measured, unaged, using a FANN 35 viscometer at several different rpm settings. The results are listed below in Table 4.

The paragraph beginning on page 36, line 24, is amended as shown below. The term "iwas," as recited on page 36, line 24 of the specification, has been replaced with "was" to correct the typographical error.

A sample of the solution ~~iwas~~was set up in a test tube and placed in a Baroid static aging cell. The sample was static aged for 16 hours at 375 °F. The sample was

then cooled to 120 °F and the same rheology test was run again to calculate plastic viscosity and the yield point. These results are listed below in Table 21.

The paragraph beginning on page 37, line 14, is amended as shown below. The second period at the end of the paragraph has been deleted.

The foregoing detailed description of preferred embodiments is intended to be exemplary of the invention and illustrative. Modifications of the embodiments disclosed and alternative embodiments will be apparent to those skilled in the art in view of the above, and all such modifications and alternatives are intended to be within the scope of appropriate ones of the following claims.:-

#### **IN THE CLAIMS**

Claim 13. (Amended) The composition of claim 1 wherein

- the polymer is at least 0.1 wt. % of the composition, and
- the alkali metal salt of carboxylic acid is at least 60.0 wt. % of the composition.

Claim 19. (Amended) The composition of claim 14 wherein the hydrophobe reactant is selected from stearyl methacrylate, lauryl methacrylate, and ethylhexyl methacrylate.